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6. AUTHOR(S)

J. E. Lawler, L. W. Anderson

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)

University of Wisconsin-Madison
Department of Physics
1150 University Avenue
Madison, WI 53706

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13. ABSTRACT *(Maximum 200 words)*

The study of the gas phase chemical and physical reactions that occur in the chemical vapor deposition (CVD) of diamond was the goal of ARO grants DAAH04-93-G-0260 and DAAH04-93-0185. We have developed an ultra-sensitive white light absorption spectroscopy technique and have used it together with absorption spectroscopy at the SRC synchrotron to determine the density of CH4, CH_3, CH_2, CH, C, and C_2H_2 and the dissociation fraction $[H]/[H_2]$ in various CVD reactors under diamond growth conditions. We have developed models to understand the gas phase reactions. We have found for different input gases with the same carbon fraction that the CH_3 and CH densities are nearly the same in a microwave CVD reactor. Gas phase reactions rapidly scramble the system. We have also found that the $[H]/[H_2]$ ratio is determined by the dissociation fraction at the filament and that the C, CH, CH_2, CH_3 and CH_4 species are in equilibrium at the $[H]/[H_2]$ ratio and the temperature. We have developed methods to measure the gas phase temperature in CVD reactors.

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STATEMENT OF THE PROBLEM

The study of the gas phase chemical and physical reactions that occur in the chemical vapor deposition (CVD) of diamond is the primary goal of ARO Grants DAAH04-93-G-0260 and DAAH04-93-G-0185. In particular the goal is the determination of what molecules and free radicals are produced in different types of CVD reactors. The densities of these molecules and free radicals as a function of position in the reactor are to be determined for different feed gases and the relationship of the gas phase molecules and radicals to the growth of diamond is to be determined.

SUMMARY OF IMPORTANT RESULTS

The goal of our investigations carried out under ARO grants number DAAH04-93-G-0260 and DAAH04-93-G-0185 is the development of a detailed understanding of the microscopic physics and chemistry of the chemical vapor deposition (CVD) of diamond films.

During this grant we have constructed a microwave discharge CVD reactor and have used it together with our hot filament and dc discharge CVD reactors for absorption spectroscopy experiments to study the gas phase reactions important in the CVD of diamond films.

We have developed an ultra-sensitive white light absorption spectroscopy technique. This is an important new diagnostic tool for use in CVD systems. This technique has enabled us to measure the absolute column densities of free radicals and molecules such as CH, CH_3, and C_2H_2 in the gas phase in our diamond CVD reactors. The apparatus for the high sensitivity absorption spectroscopy works as follows. The broad bandwidth light from an ultra-stable high pressure Xe or D_2 lamp is used as the white light source. The light from this lamp is imaged at the center of the CVD reactor and then reimaged at the entrance slits of a half meter spectrometer. The spectrometer disperses the broad bandwidth light. The light at the output of the spectrometer is detected by the use of a diode array. Our current setup can be used to detect light with wavelengths from the VUV to the near IR. This system is very sensitive. We have detected absorptances smaller than 10^{-5}. Our new technique has two major advantages over older single channel absorption spectroscopy techniques: (1) Because a wide range of wavelengths are detected simultaneously the experiment is relatively insensitive to fluctuations and drifts in the light output from the white light source. (2) Because a wide range of wavelengths are detected simultaneously photon statistics are accumulated rapidly. This new technique has been used with a hot filament CVD reactor, a dc discharge CVD reactor, and a microwave discharge CVD reactor. The use with the dc and microwave discharge reactors is especially remarkable since the discharges emit light at the wavelengths of the absorption feature. It is possible to use digital storage for the signals with the discharge on and off and then use digital subtraction to discriminate against the light emitted by the discharge. Thus one can detect only the white light continuum even in the presence of the radiating plasma. Forming the ratio of the intensity of the white light continuum after passage through the absorbing medium to the intensity of the white light continuum in the absence of the absorbing medium yields the transmittance (one minus the absorptance) of the absorbing medium. As stated we have detected absorptances smaller than 10^{-5}.

We have used the ultra-sensitive white light absorption spectroscopy to measure the column density of CH_3, CH, and C_2H_2 in the various CVD reactors. Our method for monitoring CH_3 densities during CVD of diamond uses the UV absorption feature of CH_3 at 216 nm. The sensitivity and simplicity of our experiment gives it huge advantages over competing techniques for detecting CH_3. We monitor the CH and C_2H_2 densities using absorption bands for these molecules.

During this grant we have completed an extensive series of experiments on alternate feed gas mixtures including ethane (C_2H_6) in H_2, propane (C_3H_8) in H_2, ethylene (C_2H_4) in H_2, and methane (CH_4) and oxygen (O_2) in H_2. These experiments have used the high sensitivity absorption spectroscopy technique. The remarkable result found in these experiments is that the CH_3 and CH densities and the diamond growth rate are independent of the input gases. The rapid gas phase reactions completely chemically scramble the system so that the identity of the input gases is of little significance in the CVD of diamond provided the hot filament is not poisoned.

During this grant period we have developed a method of measuring the hydrogen dissociation ratio, $[H]/[H_2]$, or ratio of atomic H density to molecular H_2 density. Atomic H is particularly important as it performs several roles including the following: (i) driving the gas phase chemistry, (ii) preferentially etching non-diamond deposits (iii) stabilizing the diamond surface during growth, and (iv) opening growth sites. Our method for measuring $[H]/[H_2]$ involves measuring both the CH_3 and CH densities. We measure [CH] using absorption on either the $A^2\Delta \leftarrow X^2\Pi(0,0)$ band near 432 nm or the $C^2\Sigma^+ \leftarrow X^2\Pi(0\text{-}0)$ band near 314 nm. The extraordinary sensitivity achieved using our experiment is essential for these measurements. The dissociation ratio, $[H]/[H_2]$, is extracted from $[CH_3]$ and [CH] using the fact that the abstraction reactions and (1) ($CH_3 + H \leftrightharpoons HC_2 + H_2$ and (2) $CH_2 + H \leftrightharpoons CH + H_2$ are rapid enough to reach partial local thermodynamic equilibrium under typical (20 Torr) diamond CVD conditions. The dissociation ratio is

$$[H]/[H_2] = \sqrt{\frac{[CH]}{K_1(T)K_2(T)[CH_3]}}$$

where $K_1(T)$ and $K_2(T)$ are equilibrium constants for reaction 1 and 2. Although we still plan to do a more direct absorption experiment at Lyman alpha to measure [H], we are very optimistic that the $[CH]/[CH_3]$ method described above is reliable. The simplicity of the $[CH]/[CH_3]$ method will make it an important and widely used method for determining $[H]/[H_2]$.

We have carried out during this grant a series of single channel absorption spectroscopy experiments in the vacuum UV at the SRC synchrotron. In these experiments we have detected CH_4, CH_3, CH, C, C_2H_2, H and vibrationally excited H_2. Unfortunately the H absorption feature is very deep and is blended with other absorption features. It will be very difficult to determine the atomic H column density from experiments of this type. Fortunately we have found and confirmed an alternate method for obtaining the atomic column H density. The detection of CH_4, CH_3, CH, and C has enabled us to determine that the single C atom radicals and molecules are all in partial thermodynamic equilibrium via abstraction reactions of the form $CH_M + H \leftrightarrow CH_{M-1} + H_2$. The chemical equilibrium constants for these reactions are known so that from our measurements we are able to determine the $[H]/[H_2]$ ratio from any two of the measured single C densities. The $[H]/[H_2]$ ratios obtained from our different measurements are all the same within experimental uncertainties. Thus we now have reliable measurements of the atomic H column densities as a function of the position below the Si substrate in our hot filament CVD reactor.

We have carried out a set of measurements using a new microwave discharge CVD reactor. We have determined the conditions under which good quality diamond films can be grown using the microwave discharge reactor, and we have used high sensitivity absorption spectroscopy measurements of the densities of CH and CH_3 in the microwave discharge reactor. These experiments have allowed us to obtain not only the densities of CH_3 and CH but also the $[H]/[H_2]$ ratio for the microwave CVD reactor.

One of the most important parameters in a CVD reactor is the gas kinetic temperature since it determines reaction rates. The gas temperature is however very difficult to measure. We have measured gas temperatures using the rotational absorption spectra of H_2 in the lowest vibrational level and the first few excited vibrational levels obtained in our synchrotron experiments. This method works well but requires the use of computer filling. We have previously developed a technique for obtaining the gas temperature in the dc discharge and microwave discharge CVD reactors. This method uses the $G \leftarrow B$ radiation from the H_2 molecule in the discharge to determine the gas temperature. We have found that the

radiation from the Fulsher band in a discharge does not give a temperature. We have also studied the radiating bands of N_2 that can be used to obtain a gas kinetic temperature in a nitrogen containing discharge.

Finally we have constructed a compute code for modeling of the hot filament reactor. The computer code will include both diffusive and convective gas flow, gas phase and surface chemistry, and heat flow. The most important result from this modeling is that the $[H]/[H_2]$ ratio is primarily determined by the degree of dissociation of H_2 at the filament and that the abstraction reactions involving CH_n are in equilibrium and hence the CH_n density is determined by the $[H]/[H_2]$ ratio and the gas temperature.

LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP DURING THIS REPORTING PERIOD INCLUDING JOURNAL REFERENCES

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SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT WITH DEGREES AWARDED

J. E. Lawler (P.I.), L. W. Anderson (Co. P.I.)
M. A. Childs (received PhD in Physics) K. L. Menningen (received PhD in Physics) G. A. Parker (received PhD in Physics) A. Goyette (grad student) C. Ericson (undergrad student) J. Peck (undergrad student)